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Inorganic Chemistry Article

Synthesis and Structures of Aluminum and Magnesium Complexes of Tetraimidophosphates and Trisamidothiophosphates: EPR and DFT Investigations of the Persistent Neutral Radicals $\{Me_2Al[(\mu\text{-}NR)(\mu\text{-}N^tBu)P(\mu\text{-}N^tBu)_2]Li(THF)_2\}^{\bullet}$ (R = $SiMe_3$, ^tBu)

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Reactions of $(RNH)_3PNSiMe_3$ (**3a**, R = ^tBu; **3b**, R = Cy) with trimethylaluminum result in the formation of $\{Me_2Al(\mu\text{-}N^tBu)(\mu\text{-}NSiMe_3)P(NH^tBu)_2]\}$ (**4**) and the dimeric trisimidometaphosphate $\{Me_2Al[(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)P(\mu\text{-}NCy)_2P(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)]AlMe_2\}$ (**5a**), respectively. The reaction of $SP(NH^tBu)_3$ (**2a**) with 1 or 2 equiv of $AlMe_3$ yields $\{Me_2Al[(\mu\text{-}S)(\mu\text{-}N^tBu)P(NH^tBu)_2]\}$ (**7**) and $\{Me_2Al[(\mu\text{-}S)(\mu\text{-}N^tBu)P(\mu\text{-}NH^tBu)(\mu\text{-}N^tBu)]AlMe_2\}$ (**8**), respectively. Metalation of **4** with ^nBuLi produces the heterobimetallic species $\{Me_2Al[(\mu\text{-}N^tBu)(\mu\text{-}NSiMe_3)P(\mu\text{-}NH^tBu)(\mu\text{-}N^tBu)]Li(THF)_2\}$ (**9a**) and $\{[Me_2Al][Li]_2[P(N^tBu)_3(NSiMe_3)]\}$ (**10**) sequentially; in THF solutions, solvation of **10** yields an ion pair containing a spirocyclic tetraimidophosphate monoanion. Similarly, the reaction of $(^tBuNH)_3PN^tBu$ with $AlMe_3$ followed by 2 equiv of ^nBuLi generates $\{Me_2Al[(\mu\text{-}N^tBu)_2P(\mu_2\text{-}N^tBu)_2(\mu_2\text{-}THF)[Li(THF)]_2\}$ (**11a**). Stoichiometric oxidations of **10** and **11a** with iodine yield the neutral spirocyclic radicals $\{Me_2Al[(\mu\text{-}NR)(\mu\text{-}N^tBu)P(\mu\text{-}N^tBu)_2]Li(THF)_2\}^{\bullet}$ (**13a**, R = $SiMe_3$; **14a**, R = ^tBu), which have been characterized by electron paramagnetic resonance spectroscopy. Density functional theory calculations confirm the retention of the spirocyclic structure and indicate that the spin density in these radicals is concentrated on the nitrogen atoms of the PN_2Li ring. When **3a** or **3b** is treated with 0.5 equiv of dibutylmagnesium, the complexes $\{Mg[(\mu\text{-}N^tBu)(\mu\text{-}NH^tBu)P(NH^tBu)(NSiMe_3)]_2\}$ (**15**) and $\{Mg[(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)P(NHCy)_2]_2\}$ (**16**) are obtained, respectively. The addition of 0.5 equiv of $MgBu_2$ to **2a** results in the formation of $\{Mg[(\mu\text{-}S)(\mu\text{-}N^tBu)P(NH^tBu)_2]_2\}$ (**17**), which produces the hexameric species $\{[MgOH][(\mu\text{-}S)(\mu\text{-}N^tBu)P(NH^tBu)_2]\}_6$ (**18**) upon hydrolysis. Compounds **4**, **5a**, **7**–**11a**, and **15**–**17** have been characterized by multinuclear (^1H, ^{13}C, and ^{31}P) NMR spectroscopy and, in the case of **5a**, **9a·**2THF, **11a**, and **18**, by X-ray crystallography.

Introduction

One of the more active areas of main-group chemistry research over the past decade has been the synthesis and characterization of imido analogues of simple oxoanions such as carbonate, silicate, and phosphate.[1] The underlying principle of this work is that the oxo units $[O]^{2-}$ of these species are formally isoelectronic[2] with the imido $[NR]^{2-}$ (R = H, alkyl, aryl) group, and thus, a new class of p-block polyanions can be generated by substituting some, or all, of the oxygen atoms by imido groups. The chemical and physical properties of these polyimido anions are dependent, in large part, upon the ratio of imido/oxo units and the size of the imido substituent.[1]

Numerous analogues of phosphorus oxoanions have been prepared,[3] including the trisimido(meta)phosphate[4] $[P(NR)_3]^-$ and tetraimido(ortho)phosphate $[P(NR)_3(NR')]^{3-}$ (R = R′ =

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(1) For recent reviews, see (a) Brask, J. K.; Chivers, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3960−3976. (b) Aspinall, G. M.; Copsey, M. C.; Leedham, A. P.; Russell, C. A. *Coord. Chem. Rev.* **2002**, *227*, 217−232.

(2) The original definition of “isoelectronic” (isosteric) compounds restricts the term to species having the *same number of atoms* and the same number of electrons (Langmuir, I. *J. Am. Chem. Soc.* **1919**, *41*, 1543). Thus, according to this definition, N^{3-} is isoelectronic with O^{2-}. However, nitrides are compositionally different from oxides as a result of the different charges on the anions.

(3) Chivers, T. *Top. Curr. Chem.* **2003**, *229*, 143−159.

(4) See, for example, (a) Niecke, E.; Frost, M.; Nieger, M.; von der Gönna, V.; Ruban, A.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2111. (b) Scherer, O. J.; Quintus, P.; Kaub, J.; Sheldrick, W. S. *Chem. Ber.* **1987**, *120*, 1463. (c) Lief, G. R.; Carrow, C. J.; Stahl, L.; Staples, R. J. *Organometallics* **2001**, *20*, 1629.

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naphthyl;[5] R = ^{t}Bu, R′ = SiMe$_3$[6]) trianions. Heteroleptic systems, such as the trisimidophosphate and -thiophosphate trianions [EP(NR)$_3$]$^{3-}$ (E = O,[7] S[8]), have also been reported recently, and the first transition-metal derivatives of the sulfur-containing ligand have been characterized.[9]

Previously, we have thoroughly investigated the reactivities of a series of trisaminophosphates, OP(NH^{t}Bu)$_3$ (**1**),[6,8] SP(NHR)$_3$ (**2a**, R = ^{t}Bu; **2b**, R = ^{i}Pr; **2c**, R = *p*-tol),[8,10] and (RNH)$_3$PNSiMe$_3$ (**3a**, R = ^{t}Bu; **3b**, R = Cy),[6,11] toward alkyllithium reagents. It was found that the reactivity of these aminophosphate species increases across the series **1** < **2** < **3**. Specifically, 3-fold deprotonation of **1**, **2a**, or **2b** is not possible using *n*-butyllithium, whereas it does occur for **2c** and is readily effected for both **3a** and **3b**. More recently, we have prepared a series of zinc imidophosphates by the reactions of **1**, **2a**, **3a,** and **3b** with dimethylzinc.[7] Interestingly, the reaction of **1** with ZnMe$_2$ generated several products via at least two distinct reaction pathways, whereas the reaction of **3a** and dimethylzinc produced only {MeZn[(μ-N^{t}Bu)(μ-NSiMe$_3$)P(NH^{t}Bu)$_2$]}. In addition, two zinc complexes were isolated that contained the trisimidophosphate trianion [OP(N^{t}Bu)$_3$]$^{3-}$, which had not been observed in earlier reactions between **1** and *n*-butyllithium, trimethylaluminum, or lithium aluminum hydride.[12]

The only known main-group metal complexes of **2** and **3** are their lithium derivatives. In view of the current interest in aluminophosphates,[13] the development of synthetic routes to a family of polyimidoaluminophosphates is certainly a worthwhile endeavor. To this end, we have examined the reactions of **2a** and **3** with trimethylaluminum. While it is not possible to effect the 3-fold deprotonation of **1** with trimethylaluminum,[12] the possibility of preparing trisimido(thio)- or tetraimidoaluminophosphates remains. Reactions of **1**−**3** with MgBu$_2$ have also been investigated in order to gain a better understanding of the reactivity of these amido reagents toward metal alkyls.

Experimental Section

Reagents and General Procedures. All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, *n*-hexane, diethyl ether, and tetrahydrofuran (THF) were dried over Na/benzophenone, distilled, and stored over molecular sieves prior to use. Trimethylaluminum (2.0 M solution in toluene), ^{n}BuLi (2.5 M solution in hexanes), and MgBu$_2$ (1.0 solution in heptane) were used as received from Aldrich. Iodine was sublimed prior to use. (RNH)$_3$PNSiMe$_3$ (R = ^{t}Bu, Cy),[6] SP(NH^{t}Bu)$_3$,[8] and OP(NH^{t}Bu)$_3$[8] were prepared as described previously.

Instrumentation. ^{1}H, ^{7}Li, ^{13}C, and ^{31}P NMR spectra were collected on a Bruker DRX-400 spectrometer with chemical shifts reported relative to Me$_4$Si in CDCl$_3$ (^{1}H and ^{13}C), LiCl in D$_2$O (^{7}Li), and 85% H$_3$PO$_4$ in D$_2$O (^{31}P). All spectra were collected at 22 °C. Infrared spectra were recorded as Nujol mulls on KBr plates using a Nicolet Nexus 470 FTIR spectrometer in the range 400−4000 cm^{-1}. Electron paramagnetic resonance (EPR) spectra were recorded at 22 °C on a Bruker EMX 113 spectrometer; spectral simulations were carried out using XEMR[14] and WINEPR SimFonia.[15] Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of {Me$_2$Al[(μ-N^{t}Bu)(μ-NSiMe$_3$)P(NH^{t}Bu)$_2$]} (4). A solution of AlMe$_3$ (0.60 mL, 2.0 M, 1.2 mmol) in toluene was added to a clear, colorless solution of (^{t}BuNH)$_3$PNSiMe$_3$ (0.404 g, 1.21 mmol) in hexane (20 mL) at 22 °C. After 3 h, the solvent was removed in vacuo, and the product was washed with hexane (5 mL), leaving **4** as an off-white powder (0.339 g, 0.868 mmol, 72%). ^{1}H NMR (C$_6$D$_6$, δ): 1.8 (br, 2 H, N*H*), 1.29 (d, 9 H, N^{t}Bu), 1.16 (d, 18 H, NH^{t}Bu), 0.34 (s, 9 H, SiMe$_3$), −0.22 (s, 6 H, AlMe$_2$). ^{13}C NMR (C$_6$D$_6$, δ): 51.76 [d, N*C*Me$_3$, $^2J(^{13}\text{C-}^{31}\text{P}) = 10.9$ Hz], 50.63 [d, NH*C*Me$_3$, $^2J(^{13}\text{C-}^{31}\text{P}) = 15.2$ Hz], 33.01 [d, NC*Me*$_3$, $^3J(^{13}\text{C-}^{31}\text{P}) = 34.2$ Hz], 32.30 [d, NHC*Me*$_3$, $^3J(^{13}\text{C-}^{31}\text{P}) = 15.5$ Hz], 3.57 [d, SiMe$_3$, $^3J(^{13}\text{C-}^{31}\text{P}) = 14.9$ Hz], 1.37 (s, AlMe$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 5.6 (s). IR (Nujol): 3404 cm^{-1} (ν N−H). Anal. Calcd for C$_{17}$H$_{44}$N$_4$AlPSi: C, 52.27; H, 11.35; N, 14.34. Found: C, 52.16; H, 12.03; N, 13.92.

Preparation of {Me$_2$Al[(μ-NCy)(μ-NSiMe$_3$)P(μ-NCy)$_2$P(μ-NCy)(μ-NSiMe$_3$)]AlMe$_2$} (5a). A solution of AlMe$_3$ (0.35 mL, 2.0 M, 0.70 mmol) in toluene was added to a clear, colorless solution of (CyNH)$_3$PNSiMe$_3$ (0.286 g, 0.693 mmol) in hexane (20 mL) at 22 °C. The reaction mixture was stirred for 15 h; the volume of the solution was then reduced to 1 mL and stored at −18 °C. After 48 h, colorless crystals of **5a** were obtained (0.226 g, 0.306 mmol, 88.3%). ^{1}H NMR (C$_6$D$_6$, δ): 0.8−1.9 (m, Cy), 0.22 (s, 18 H, SiMe$_3$), −0.37 (s, 6 H, AlMe$_2$). ^{13}C NMR (C$_6$D$_6$, δ): 51.68 (s, *C*Me$_3$), 50.05 (s, *C*Me$_3$), 37.78 [d, NC*C*H$_2$, $^3J(^{13}\text{C-}^{31}\text{P}) = 35.6$ Hz], 36.91 [d, NC*C*H$_2$, $^3J(^{13}\text{C}-^{31}\text{P}) = 19.2$ Hz], 36.78 [d, NC*C*H$_2$, $^3J(^{13}\text{C-}^{31}\text{P}) = 18.4$ Hz], 26.18 (s, NCCH$_2$*C*H$_2$), 25.94 (s, NCCH$_2$*C*H$_2$), 25.78 (s, *p*-CH$_2$), 2.67 [d, SiMe$_3$, $^3J(^{13}\text{C-}^{31}\text{P}) = 14.0$ Hz], −6.81 (s, AlMe$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$, δ): 17.1 (s). CHN analyses gave high C values owing to difficulties with the complete removal of CyNH$_2$.

Preparation of {Me$_2$Al[(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]} (7). A solution of AlMe$_3$ (2.25 mL, 2.0 M, 4.5 mmol) in toluene was added to a clear, colorless solution of SP(NH^{t}Bu)$_3$ (1.24 g, 4.44 mmol) in toluene (25 mL) at 22 °C. After 24 h, the solvent was removed in vacuo, leaving a colorless oil; after storage for 12 h, the product had solidified, giving **7** as a white powder (1.25 g, 3.73 mmol, 82.8%). ^{1}H NMR (C$_6$D$_6$, δ): 1.23 (s, 9 H, N^{t}Bu), 1.18 (s, 18 H, NH^{t}Bu), −0.24 [d, $^4J(^1\text{H-}^{31}\text{P}) = 1.8$ Hz, 6 H, Me$_2$Al]. ^{13}C{^{1}H} NMR (C$_6$D$_6$, δ): 54.32 [d, *C*Me$_3$, $^2J(^{13}\text{C-}^{31}\text{P}) = 37.2$ Hz], 52.44 [d, *C*Me$_3$, $^2J(^{13}\text{C-}^{31}\text{P}) = 9.0$ Hz], 33.03 [d, C*Me*$_3$, $^3J(^{13}\text{C-}^{31}\text{P}) = 34.7$ Hz], 31.42 [d, C*Me*$_3$, $^3J(^{13}\text{C-}^{31}\text{P}) = 18.6$ Hz], −5.20 (br, Me$_2$-

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Al). ^{31}P{^{1}H} NMR (C_6D_6, δ): 35.6 (s). Anal. Calcd for $C_{14}H_{35}N_3PSAl$: C, 50.12; H, 10.52; N, 12.53. Found: C, 49.64; H, 10.97; N, 12.63.

Preparation of {Me$_2$Al[(μ-S)(μ-N^{t}Bu)P(μ-NH^{t}Bu)(μ-N^{t}Bu)]AlMe$_2$} (8). A solution of AlMe$_3$ (4.8 mL, 2.0 M, 9.6 mmol) in toluene was added to a clear, colorless solution of SP(NH^{t}Bu)$_3$ (1.30 g, 4.65 mmol) in toluene (20 mL) at 22 °C. After 40 h, the solvent was removed in vacuo, leaving **8** as a white powder (1.74 g, 4.44 mmol, 95.5%). ^{1}H NMR (C_6D_6, δ): 3.30 (br, d, N*H*), 1.33 [d, $^4J(^1H\text{-}^{31}P) = 0.9$ Hz, 9 H, N^{t}Bu], 1.23 [d, $^4J(^1H\text{-}^{31}P) = 0.7$ Hz, 9 H, N^{t}Bu], 1.20 [d, $^4J(^1H\text{-}^{31}P) = 0.9$ Hz, 9 H, NH^{t}Bu], −0.25 (s, 3H, Me$_2$Al), −0.31 (s, 3 H, Me$_2$Al), −0.39 (s, 3H, Me$_2$Al), −0.54 (s, 3 H, Me$_2$Al). ^{13}C{^{1}H} NMR (C_6D_6, δ): 59.09 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 12.9$ Hz], 54.99 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 39.3$ Hz], 53.53 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 8.8$ Hz], 33.23 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 34.0$ Hz], 32.33 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 31.2$ Hz], 30.05 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 17.9$ Hz], −5.20 (br, Me$_2$Al), −6.09 (br, Me$_2$Al). ^{31}P{^{1}H} NMR (C_6D_6, δ): 40.9 (s). Anal. Calcd for $C_{16}H_{40}N_3PSAl_2$: C, 49.08; H, 10.30; N, 10.73. Found: C, 49.05; H, 10.72; N, 10.97.

Preparation of {[Me$_2$Al][Li][P(N^{t}Bu)$_2$(NH^{t}Bu)(NSiMe$_3$)]} (9a). A solution of AlMe$_3$ (0.75 mL, 2.0 M, 1.50 mmol) in toluene was added to a stirred solution of (^{t}BuNH)$_3$PNSiMe$_3$ (0.502 g, 1.50 mmol) in hexane (20 mL) at 22 °C. After 1.5 h, ^{n}BuLi (0.60 mL, 1.50 mmol) was added, resulting in a white slurry. After an additional 3 h, the solvent was removed in vacuo, leaving **9a** as a white powder (0.582 g, 1.47 mmol, 98%). Colorless X-ray quality crystals of {Me$_2$Al[(μ-N^{t}Bu)(μ-NSiMe$_3$)P(μ-NH^{t}Bu)(μ-N^{t}Bu)]Li(THF)$_2$} (**9a**·2THF) were obtained from a THF/hexane mixture at −18 °C. ^{1}H NMR (d_8-THF, δ): 1.35 (s, 9 H, ^{t}Bu), 1.31 (s, 9 H, ^{t}Bu), 1.29 (s, 9 H, ^{t}Bu), 0.13 (s, 9 H, SiMe$_3$), −0.89 (d, 6 H, Me$_2$Al). ^{13}C{^{1}H} NMR (d_8-THF, δ): 52.39 (s, *C*Me$_3$), 51.14 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 36.3$ Hz], 36.70 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 38.7$ Hz], 36.09 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 41.1$ Hz], 34.11 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 29.1$ Hz], 33.50 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 19.2$ Hz], 14.59 (s, SiMe$_3$), 4.26 (s, AlMe$_2$). ^{31}P{^{1}H} NMR (d_8-THF, δ): 8.2 (s). Anal. Calcd for $C_{17}H_{43}N_4LiAlSiP$: C, 51.49; H, 10.93; N, 14.13. Found: C, 50.90; H, 10.73; N, 14.31.

Preparation of {[Me$_2$Al][Li]$_2$[P(N^{t}Bu)$_3$(NSiMe$_3$)]} (10). A solution of AlMe$_3$ (0.60 mL, 2.0 M, 1.2 mmol) in toluene was added to a stirred pale yellow solution of (^{t}BuNH)$_3$PNSiMe$_3$ (0.404 g, 1.21 mmol) in hexane, resulting in a cloudy off-white solution. After 3h, ^{n}BuLi (0.90 mL, 2.5 M, 2.3 mmol) in hexanes was added to the reaction mixture, resulting in a white slurry. After an additional 3 h, the solvent was removed in vacuo, leaving **10** as a white powder (0.427 g, 1.06 mmol, 93%). ^{1}H NMR (d_8-THF, δ): 1.32 (s, 9 H, N^{t}Bu), 1.30 (s, 18 H, N^{t}Bu), 0.08 (s, 9 H, SiMe$_3$), −0.94 (s, 6 H, AlMe$_2$). ^{7}Li (d_8-THF, δ): 0.70 (s). ^{7}Li (C_6D_6, δ): 1.44 (s), −2.71 (s). ^{13}C{^{1}H} NMR (C_6D_6, δ): 50.72 [d, N*C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 6.8$ Hz], 36.58 [d, NC*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 36.2$ Hz], 33.77 [d, NHC*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 27.2$ Hz], 4.19 (s, SiMe$_3$), −4.61 (s, AlMe$_2$). ^{31}P{^{1}H} NMR (d_8-THF, δ): 10.0 (s). Satisfactory CHN analyses could not be obtained because of the extremely hygroscopic nature of this compound.

Preparation of {Me$_2$Al[(μ-N^{t}Bu)$_2$P(μ$_2$−N^{t}Bu)$_2$(μ$_2$-THF)[Li(THF)]$_2$} (11a). A solution of AlMe$_3$ (0.55 mL, 2.0 M, 1.10 mmol) in toluene was added to a stirred clear, colorless solution of (^{t}BuNH)$_3$PN^{t}Bu (0.353 g, 1.11 mmol) in hexane (15 mL), resulting in an opaque white solution. After 3 h, ^{n}BuLi (1.4 mL, 1.6 M, 2.24 mmol) in hexanes was added to the reaction mixture, resulting in a white slurry. After an additional 2.5 h, the white solid was allowed to settle, and the supernatant liquid was decanted. The product was washed with an additional 5 mL of hexane prior to the removal of the solvent in vacuo. The product {[Me$_2$Al][Li]$_2$[P(N^{t}Bu)$_4$]} was isolated as a white powder (0.339 g, 0.887 mmol, 80%). Recrystallization from THF/hexane produced colorless X-ray quality crystals of {Me$_2$Al[(μ-N^{t}Bu)$_2$P(μ$_2$-N^{t}Bu)$_2$(μ$_2$-THF)[Li(THF)]$_2$} (**11a**). ^{1}H NMR (d_8-THF, δ): 1.34 (s, 36 H, N^{t}Bu), −0.96 (s, 6 H, AlMe$_2$). ^{7}Li (d_8-THF, δ): 1.23 (s). ^{13}C{^{1}H} NMR (C_6D_6, δ): 50.90 (s, N*C*Me$_3$), 50.78 [d, N*C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 8.3$ Hz], 36.41 [d, NC*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 34.9$ Hz], 34.45 [d, NHC*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 25.4$ Hz], −4.0 (br, s, AlMe$_2$). ^{31}P{^{1}H} NMR (d_8-THF, δ): 12.4 (s). Satisfactory CHN analyses could not be obtained because of the extremely hygroscopic nature of this compound.

Preparation of {Mg[(μ-N^{t}Bu)(μ-NH^{t}Bu)P(NH^{t}Bu)(NSiMe$_3$)]$_2$} (15). A solution of MgBu$_2$ (1.56 mL, 1.0 M, 1.56 mmol) in heptane was added to a stirred solution of (^{t}BuNH)$_3$PNSiMe$_3$ (1.05 g, 3.14 mmol) in hexane (15 mL) at 22 °C. After 18 h, the solvent was removed in vacuo, leaving **15** as a white solid (0.986 g, 1.42 mmol, 91%). ^{1}H NMR (C_6D_6, δ): 1.9 (br, d, NH), 1.8 (br, d, NH), 1.49 (s, 9 H, N^{t}Bu), 1.39 (s, 9 H, NH^{t}Bu), 1.32 (s, 9 H, NH^{t}Bu), 0.50 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR (d_8-THF, δ): 51.52 (s, *C*Me$_3$), 51.46 (s, *C*Me$_3$), 51.40 (s, *C*Me$_3$), 50.89 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 3.0$ Hz], 50.63 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 15.0$ Hz], 35.2 (s, C*Me*$_3$), 33.4 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 30.0$ Hz], 33.2 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 30.0$ Hz], 32.3 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 30.0$ Hz], 5.7 [d, SiMe$_3$, $^3J(^{13}C\text{-}^{31}P) = 30.0$ Hz], 4.3 [d, SiMe$_3$, $^3J(^{13}C\text{-}^{31}P) = 30.0$ Hz]. ^{31}P{^{1}H} NMR(C_6D_6, δ): 5.2 (s). Anal. Calcd for $C_{30}H_{76}N_8MgP_2Si_2$: C, 52.11; H, 11.08; N, 16.21. Found: C, 52.20; H, 10.19; N, 15.51.

Preparation of {Mg[(μ-NCy)(μ-NSiMe$_3$)P(NHCy)$_2$]$_2$} (16). A solution of MgBu$_2$ (0.82 mL, 0.82 mmol) in heptane was added to a stirred solution of (CyNH)$_3$PNSiMe$_3$ (0.677 g, 1.64 mmol) in hexane (20 mL) at 22 °C. After 20 h, the solvent was removed in vacuo, leaving **16** as an off-white solid (0.540 g, 0.637 mmol, 78%). ^{1}H NMR (C_6D_6, δ): 1.0−3.2 (br, m, Cy), 0.40 (s, 9 H, SiMe$_3$). ^{13}C{^{1}H} NMR (d_8-THF, δ): 52.71 (s, *C*N), 50.03 [d, *C*NH, $^2J(^{13}C\text{-}^{31}P) = 30.4$ Hz], 40.26 (s, *C*H$_2$CN), 37.70 [d, *C*H$_2$CNH, $^3J(^{13}C\text{-}^{31}P) = 80.0$ Hz], 26.73 (s, CH*C*H$_2$), 26.31 (br, s, CH$_2$*C*HCH$_2$), 4.34 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (C_6D_6, δ): 19.6 (s). Anal. Calcd for $C_{42}H_{88}N_8P_2Si_2Mg$: C, 59.51; H, 10.46; N, 13.22. Found: C, 59.46; H, 10.88; N, 12.53.

Preparation of {Mg[(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]$_2$} (17). A solution of MgBu$_2$ (2.0 mL, 1.0 m, 2.0 mmol) was added to a stirred solution of SP(NH^{t}Bu)$_3$ (1.125 g, 4.026 mmol) in toluene (20 mL) at 22 °C, resulting in a clear, colorless solution. After 20 h, the solvent was removed in vacuo, leaving a colorless oil. After storage for 24 h, **17** was obtained as a white powder (1.077 g, 1.850 mmol, 92.5%). ^{1}H NMR(C_6D_6, δ): 2.03 (br, d, N*H*), 1.42 (s, 9H, N^{t}Bu), 1.30 (s, 18H, NH^{t}Bu).^{13}C{^{1}H} NMR (C_6D_6, δ): 53.32 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 46.7$ Hz], 51.76 [d, *C*Me$_3$, $^2J(^{13}C\text{-}^{31}P) = 8.8$ Hz], 34.73 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 41.0$ Hz], 31.63 [d, C*Me*$_3$, $^3J(^{13}C\text{-}^{31}P) = 16.9$ Hz]. ^{31}P{^{1}H} NMR (C_6D_6, δ): 38.8 (s). Anal. Calcd for $C_{24}H_{58}N_6P_2S_2Mg$: C, 49.60; H, 10.06; N, 14.46. Found: C, 50.89; H, 10.62; N, 13.69.

Storage of a solution of **17** in diethyl ether at −18 °C for one week yielded colorless crystals of {[MgOH][(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]}$_6$ (**18**).

X-ray Analyses. Colorless crystals of **5a**, **9a**·2THF, **11a**, and **18** were coated with Paratone 8277 oil and mounted on a glass fiber. All measurements were made on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation. Crystallographic data are summarized in Table 1. The structures were solved by direct methods[16] and refined by full-matrix least-

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(16) Altomare, A.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

Table 1. Crystallographic Data

	5a	**9a**·2THF	**11a**	**18**
formula	$C_{34}H_{74}Al_2N_6P_2Si_2$	$C_{25}H_{59}AlLiN_4O_2PSi$	$C_{34}H_{74}AlLi_2N_4O_4P$	$C_{40}H_{100}Mg_3N_9O_4P_3S_3$
fw, g	739.07	540.74	674.80	1033.31
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a, Å	20.400(6)	10.209(3)	10.876(2)	14.993(4)
b, Å	16.813(4)	17.616(4)	12.901(3)	15.285(4)
c, Å	12.865(11)	18.975(6)	29.422(7)	15.535(4)
α, deg	90	90	90	96.188(14)
β, deg	92.31(3)	91.218(9)	91.541(13)	102.701(16)
γ, deg	90	90	90	117.474(14)
V, Å^3	4409(4)	3411.7(17)	4126.7(16)	2989.9(14)
Z	4	4	4	2
T, K	173(2)	173(2)	100(2)	173(2)
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
d_{calcd}, g cm^{-3}	1.113	1.053	1.086	1.148
μ, mm^{-1}	0.223	0.17	0.125	0.278
F(000)	1616	1192	1488	1128
R^a	0.044,	0.081	0.23	0.042
$R_w{}^b$	0.107	0.203	0.55	0.096

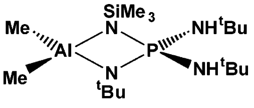
^{a} $R = [\Sigma||F_o| - |F_c||]/[\Sigma |F_o|]$ for reflections with $I > 2.00\sigma(I)$. ^{b} $R_w = \{[\Sigma w(F_o{}^2 - F_c{}^2)^2]/[\Sigma w(F_o{}^2)^2]\}^{1/2}$ for all reflections.

squares methods using SHELXL-97.[17] Hydrogen atoms were included at geometrically idealized positions and were not refined; the non-hydrogen atoms were refined anisotropically. A cyclohexyl ring in **5a** was disordered in one of the molecules; this was included in the refinements using partial site occupancy factors. Only some of the non-hydrogen atoms in **9a**·2THF were refined anisotropically. The α carbon of the N^{t}Bu group and the silicon atom of the $NSiMe_3$ group chelated to the Al atom showed positional disorder with the two atoms occupying the same sites; the model was refined with the C and Si atoms assigned partial occupancies that summed to unity. Carbon atoms of both THF ligands were disordered over two sites with equal site occupancy factors. The hydrogen atom attached to N(4) was located from a difference map.

Computational Details. The structures of the model radicals $\{Me_2Al[(\mu\text{-}NMe)(\mu\text{-}NSiH_3)P(\mu\text{-}NMe)_2]Li(OMe_2)_2\}^{\bullet}$ (**13b**) and $\{Me_2Al[(\mu\text{-}NMe)_2P(\mu\text{-}NMe)_2]Li(OMe_2)_2\}^{\bullet}$ (**14b**) were optimized in their doublet ground states using density functional theory (DFT) and C_s and C_{2v} symmetry, respectively. A hybrid PBE0 exchange-correlation functional[18,19] and Ahlrichs' triple-ζ valence basis set augmented by one set of polarization functions (TZVP)[20] were used in the optimizations. Hyperfine coupling constants (HFCCs) were then calculated by single-point calculations employing the optimized geometries, PBE0 functional, and unrestricted Kohn−Sham formalism. For P, N, Li, and Al, the single-point calculations utilized the IGLO-III basis set[21] in a completely uncontracted form and were augmented with one additional steep s function as well as f-polarization functions from the cc-pVTZ basis set.[21] For Si, C, and H, the calculations utilized the cc-pVTZ basis set[21] in its standard form. A pruned (99 590) integration grid was used in all single-point calculations to ensure numerical convergence of calculated HFCCs. All geometry optimizations were done with the Turbomole 5.7[22] program package; Gaussian 03[23] was used in all single-point calculations.

Results and Discussion

Synthesis and Characterization of $\{Me_2Al[(\mu\text{-}N^tBu)(\mu\text{-}NSiMe_3)P(NH^tBu)_2]\}$ (4) and $\{Me_2Al[(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)P(\mu\text{-}NCy)_2P(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)]AlMe_2\}$ (5a). The reaction of $(^tBuNH)_3PNSiMe_3$ (**3a**) with trimethylaluminum in a 1:1 molar ratio results in the elimination of 1 equiv of methane and the formation of $\{Me_2Al[(\mu\text{-}N^tBu)(\mu\text{-}NSiMe_3)P(NH^tBu)_2]\}$ (**4**) in good yield. On the basis of NMR data, complex **4** is assigned a monocyclic structure in which the aluminum center is chelated by the two imido groups (N^{t}Bu and $NSiMe_3$) of the monoanionic ligand (formally isoelectronic with $[H_2PO_4]^{2-}$), whereas the two NH^{t}Bu groups are in exocyclic positions. The ^{1}H NMR spectrum of **4** in C_6D_6 contains two ^{t}Bu resonances at 1.16 and 1.29 ppm (relative intensities 2:1), attributed to the NH^{t}Bu and N^{t}Bu groups, respectively. Resonances due to the $SiMe_3$ and $AlMe_2$ units with the appropriate intensities are observed at 0.34 and −0.22 ppm, respectively. The ^{13}C NMR spectrum of **4** exhibits resonances for two types of ^{t}Bu groups, one $SiMe_3$ group, and an $AlMe_2$ unit, consistent with this structural proposal; the ^{31}P spectrum reveals a singlet at 5.6 ppm. Single crystals of **4** could not be obtained owing to its high solubility in organic solvents.



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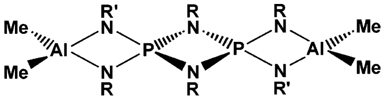

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Interestingly, the reaction of the cyclohexyl derivative $(CyNH)_3PNSiMe_3$ (**3b**) with $AlMe_3$ proceeds in a different manner. In this case, elimination of 1 equiv of cyclohexylamine results in the nearly quantitative formation of $\{Me_2Al[(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)P(\mu\text{-}NCy)_2P(\mu\text{-}NCy)(\mu\text{-}NSiMe_3)]AlMe_2\}$ (**5a**). An X-ray structure of **5a** revealed a centrosymmetric dimer in which the central feature is an essentially planar P_2N_2 ring with the two phosphorus atoms linked by NCy groups (Figure 1). Complex **5a** is the dimethylaluminum derivative of the trisimidometaphosphate monoanion $[P(NCy)_2(NSiMe_3)]^-$. Two closely related com-

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[17] Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.

[18] (a) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865−3868. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1997**, *78*, 1396−1396 (E).

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[20] The TZVP basis set was used as it is referenced in the Turbomole 5.7 internal basis set library.

[21] The basis set was taken from the EMSL basis set library: http://www.emsl.pnl.gov/forms/basisform.html (accessed December 2004).

[22] *TURBOMOLE*, version 5.7. R. Theoretical Chemistry Group, University of Karlsruhe: Karlsruhe, Germany, 2004.

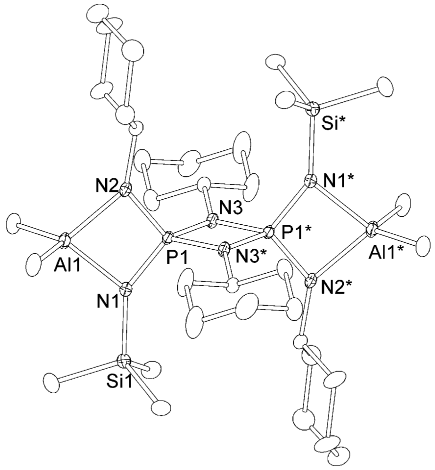


Figure 1. Thermal ellipsoid diagram of **5a** (30% probability ellipsoids). Hydrogen atoms omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **5a**[a]

P(1)−N(1)	1.5903(15)	P(1)−N(2)	1.5952(15)
P(1)−N(3)	1.6816(16)	Al(1)−C(4)	1.959(2)
Al(1)−C(5)	1.963(2)	Al(1)−N(1)	1.9597(16)
Al(1)−N(2)	1.9251(16)	P(1)−N(3)−P(1)*	96.55(9)
N(3)−P(1)−N(3)*	83.45(9)	N(1)−Al(1)−N(2)	76.40(6)
P(1)−N(1)−Al(1)	92.27(7)	P(1)−N(2)−Al(1)	93.41(7)

[a] Symmetry transformations used to generate equivalent atoms: #1 −*x*, −*y*, −*z*; #2 −*x* + 1, −*y*, −*z* + 1.

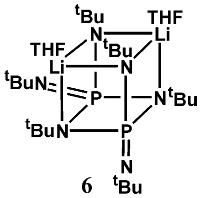
plexes have been isolated by Stahl et al.[4c] from the reaction of the bis(amino)cyclodiphosph(V)azanes *cis*-{(^{t}BuNH)-(RN=PN^{t}Bu)$_2$(NH^{t}Bu)} with trimethylaluminum. The general structure of these tricyclic species is shown above (**5a**, R = Cy, R′ = SiMe$_3$; **5b**, R = ^{t}Bu, R′ = Ph; **5c**, R = ^{t}Bu, R′ = *p*-tol).

Selected bond lengths and bond angles of **5a** are shown in Table 2. Each phosphorus atom is also part of a planar four-membered PN$_2$Al ring that is approximately perpendicular to the P$_2$N$_2$ ring. The dimethylaluminum cations are chelated by an NSiMe$_3$ group and the NCy group that is not involved in the central P$_2$N$_2$ ring. The P−N distances involving these two imido ligands are very similar [P(1)−N(1) = 1.5903(15) Å; P(1)−N(2) = 1.5952(15) Å] despite their different substituents. These bond lengths are significantly shorter than those in the P$_2$N$_2$ ring [P(1)−N(3) = 1.6816(16) Å], indicating a higher formal bond order in the former. The two Al−N bond lengths also differ slightly [Al(1)−N(1) = 1.9597(16) Å; Al(1)−N(2) = 1.9251(16) Å], with the shorter bond observed in the case of the more basic NCy ligand.

A comparison of structural parameters of **5a** and **5c**[4c] shows the expected similarities, with P−N single bond distances of 1.701(2) Å observed within the P$_2$N$_2$ ring of **5c** [cf. 1.6816(16) Å in **5a**] and the Al−N distances in **5a** [av = 1.942(2) Å] slightly shorter than the average bond length in **5c** [1.958(2) Å]. Conversely, longer Al−C distances are observed in **5a** [1.961(2) Å] compared to those in **5c** [1.944(2) Å]. These minor differences can be attributed to the more electron-donating character of the cyclohexylimido substituents of **5a** as compared to the NR (R = ^{t}Bu, *p*-tol) groups of **5c**.

The NMR spectra of **5a** in C$_6$D$_6$ are consistent with the retention of its dimeric structure in solution. In particular, the ^{13}C NMR spectrum contained two sets of cyclohexyl resonances as well as signals attributed to the SiMe$_3$ (2.67 ppm) and AlMe$_2$ (−6.81 ppm) fragments. The ^{31}P NMR signal for **5a** appears at 17.1 ppm. While the yields involved in the two-step syntheses of the imidometaphosphate dimers **5b** and **5c** range from moderate to excellent,[4c,24] the preparation of **5a** requires only one step and does not involve the use of potentially explosive organic azides.

Synthesis and NMR Characterization of {Me$_2$Al[(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]} (7) and {Me$_2$Al[(μ-S)(μ-N^{t}Bu)P(μ-NH^{t}Bu)(μ-N^{t}Bu)]AlMe$_2$} (8). In earlier attempts[8] to prepare a trisimido(thio)phosphate trianion [SP(NR)$_3$]$^{3-}$, it was found that the reaction of SP(NH^{t}Bu)$_3$ (**2a**) with 2 equiv of *n*-butyllithium results in the extrusion of sulfur and the formation of the cubic tris(imido)metaphosphate dimer {[μ_3-Li(THF)][P(μ_3-N^{t}Bu)$_2$(N^{t}Bu)]}$_2$ (**6**) in 15% yield. In light of the results described earlier, investigations into the reactions of trisamino(thio)phosphates SP(NHR)$_3$ (**2**) with AlMe$_3$ are of considerable interest, as three possible reaction pathways can be envisioned: (i) monodeprotonation of **2** to yield a [Me$_2$Al]$^+$ complex of the [SP(NR)(NHR)$_2$]$^-$ anion, (ii) deprotonation and loss of RNH$_2$ to yield a bis(imido)-(thio)metaphosphate [SP(NR)$_2$]$^-$ monoanion, or (iii) deprotonation and sulfur extrusion to generate a tris(imido)-metaphosphate [P(NR)$_3$]$^-$ complex.



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The reaction of SP(NH^{t}Bu)$_3$ (**2a**) with 1 equiv of AlMe$_3$ results in the formation of **7**, a white powder, which has been characterized by multinuclear NMR spectroscopy. The ^{31}P NMR spectrum of the product in C$_6$D$_6$ contained a single resonance at 35.6 ppm (cf. 46.3 ppm for **2a**), a strong indication that a loss of sulfur has not occurred, since this would be accompanied by a significant upfield shift as is

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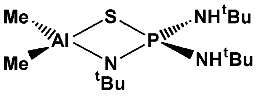
(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(24) Moser, D. F.; Carrow, C. J.; Stahl, L.; Staples, R. J. *J. Chem. Soc., Dalton Trans.* **2001**, *8*, 1246−1252.

observed for **6** (^{31}P NMR: -21 ppm).[8] The ^{1}H NMR spectrum displayed two *tert*-butyl signals at 1.23 and 1.18 ppm in a 1:2 ratio, along with a peak at -0.24 ppm attributed to a Me_2Al^+ cation; the corresponding signals were observed in the ^{13}C NMR spectrum. These NMR data are consistent with the formation of {$Me_2Al[(\mu\text{-}S)(\mu\text{-}N^tBu)P(NH^tBu)_2]$} (**7**), a monocyclic species that is isostructural with **4** and, like **4**, is the product of a simple deprotonation reaction.



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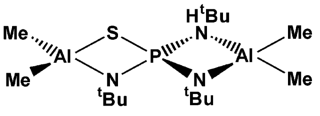

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The reaction of **2a** with 2 equiv of $AlMe_3$ yields a white powder that has been identified as the spirocyclic complex {$Me_2Al[(\mu\text{-}S)(\mu\text{-}N^tBu)P(\mu\text{-}NH^tBu)(\mu\text{-}N^tBu)]AlMe_2$} (**8**) on the basis of multinuclear NMR data. A single ^{31}P resonance was observed at 40.9 ppm, indicating that the P$-$S bond remains intact (vide supra). The ^{1}H NMR spectrum in C_6D_6 contained three *tert*-butyl resonances of equal intensities, as well as four signals between -0.54 and -0.25 ppm attributed to the methyl groups of the two inequivalent dimethylaluminum cations. The corresponding ^{t}Bu signals were observed in the ^{13}C NMR spectrum, along with two broad resonances assigned to the Me_2Al^+ cations. The fact that the four methyl groups resonate at different ^{1}H NMR frequencies is attributed to the lack of planarity in both the AlSNP and AlN_2P rings, resulting in a molecule with only C_1 symmetry.

Further investigations of the reaction of **2a** with $AlMe_3$ as a function of stoichiometry, reaction time, and reaction temperature did not yield any products other than **7** and **8**. Similarly, attempts to form a methylaluminum complex of the amidotris(imido)phosphate dianion $[P(NH^tBu)(N^tBu)_2(NSiMe_3)]^{2-}$ by increasing the reaction time and temperature or changing the stoichiometry of the reagents were not successful; in all cases, only **4** was obtained. The nearly quantitative formation of the simple dimethylaluminum derivatives **4**, **7**, and **8** is in sharp contrast to our observations for the reactions of $OP(NH^tBu)_3$ (**1**) with $AlMe_3$ in which products involving monoanionic and dianionic ligands, as well as the neutral ligand **1**, were obtained.[12]

Synthesis and NMR Characterization of {$Me_2Al[(\mu\text{-}N^tBu)(\mu\text{-}NSiMe_3)P(\mu\text{-}NH^tBu)(\mu\text{-}N^tBu)]Li(THF)_2$} (9a·2THF), {$[Me_2Al][Li]_2[P(N^tBu)_3(NSiMe_3)]$} (10), and {$Me_2Al[(\mu\text{-}N^tBu)_2P(\mu 2\text{-}N^tBu)_2(\mu\text{-}THF)][Li(THF)]_2$} (11a); X-ray Structures of 9a·2THF and 11a. In view of the limited reactivity of $AlMe_3$ toward $(^tBuNH)_3PNSiMe_3$ (**3a**), deprotonation of the dimethylaluminum complex **4** with ^{n}BuLi was investigated. The treatment of **4** with 1 equiv of ^{n}BuLi resulted in the isolation of the heterobimetallic complex {$[Me_2Al][Li][P(N^tBu)_2(NH^tBu)(NSiMe_3)]$} (**9a**) in essentially quantitative yield. Recrystallization of **9a** from THF/hexane produced colorless crystals of **9a**·2THF; an X-ray structure (Figure 2) revealed that this complex exists as the spirocycle {$Me_2Al[(\mu\text{-}N^tBu)(\mu\text{-}NSiMe_3)P(\mu\text{-}NH^tBu)(\mu\text{-}N^tBu)]Li(THF)_2$} in which the dimethylaluminum cation is *N,N′*-chelated by the $NSiMe_3$ group and one N^{t}Bu unit, while the lithium cation is coordinated to the remaining N^{t}Bu and NH^{t}Bu groups and to two molecules of tetrahydrofuran. Pertinent bond lengths and angles are given in Table 3 and are in good agreement with metrical parameters calculated for the model system {$Me_2Al[(\mu\text{-}NMe)(\mu\text{-}NSiH_3)P(\mu\text{-}NHMe)(\mu\text{-}NMe)]Li(OMe_2)_2$} (**9b**·2OMe$_2$), particularly when the difference in the identities of the imido groups is taken into account.

The P$-$N distances in **9a**·2THF range from 1.588(3) to 1.716(3) Å, with identical bond lengths of 1.640(4) Å observed for the two nitrogen atoms that chelate the aluminum center. A longer P$-$N distance is present between the phosphorus and the *tert*-butylamido nitrogen [1.716(3) Å], while a significantly shorter distance is found for the P$=$N^{t}Bu bond [1.588(3) Å], indicating the presence of localized single and double phosphorus$-$nitrogen bonds for N(4) and N(3), respectively. The mean Al$-$N distance in **9a**·2THF [1.899(4) Å] is slightly shorter than that observed in **5a** [1.9422(2) Å], presumably because of the larger formal charge on each of the chelating imido groups of **9a**·2THF as compared to those of **5a**. As expected, the Li$-$N bond to the monanion NH^{t}Bu ligand [2.178(7) Å] is substantially longer than the Li$-$N linkage involving the dianionic N^{t}Bu ligand [1.969(7) Å]. The angles about these two nitrogen atoms are also significantly different [$\angle PN(3)Li = 100.6(3)°$; $\angle PN(4)Li = 88.9(2)°$] because of their different hybridizations. In consequence, while the four-membered AlN_2P ring is essentially planar [$\angle N(1)Al(1)N(2)P(1) = -1.15(15)°$], the LiN_2P ring is puckered [$\angle N(4)P(1)N(3)Li(1) = 17.9(3)°$]. This X-ray structure confirmed the coordination mode of the ligand to the $AlMe_2$ unit of **4** that was deduced from the NMR data (vide supra).

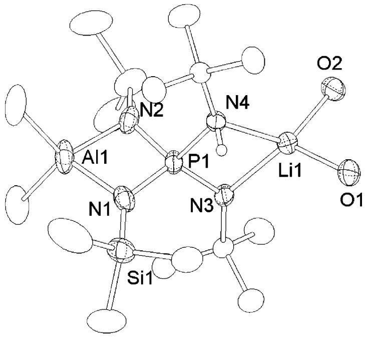


Figure 2. Thermal ellipsoid diagram of **9a**·2THF (30% probability ellipsoids). Only α-carbon atoms of the ^{t}Bu and $SiMe_3$ groups are shown; only oxygen atoms of the THF molecules are shown.

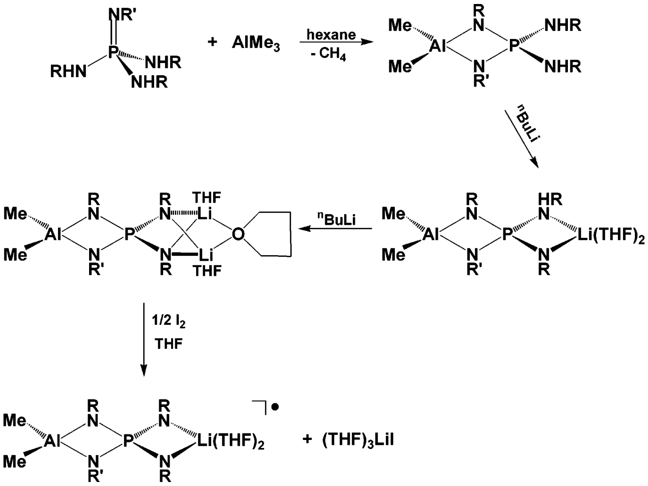
The ^{1}H NMR spectrum of **9a** in d_8-THF contains three ^{t}Bu signals of equal intensity at 1.35, 1.31, and 1.29 ppm, as well as a single $SiMe_3$ resonance at 0.13 ppm and a singlet at -0.89 ppm due to the two equivalent methyl groups of the $AlMe_2$ unit. The corresponding signals were observed in the ^{13}C NMR spectrum, while a single resonance at 8.2 ppm was observed in the ^{31}P NMR spectrum. These spectroscopic data are consistent with the retention of the spirocyclic structure of **9a**·2THF in THF solution.

In a similar manner, the dilithiated complex {$[Me_2Al][Li]_2[P(N^tBu)_3(NSiMe_3)]$} (**10**) is recovered in excellent yield from the reaction of **4**, prepared in situ, with 2 equiv of ^{n}BuLi (Scheme 1). An analogous synthesis of the sym-

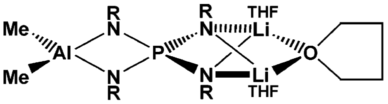
Table 3. Selected Bond Lengths (Å) and Angles (deg) for **9**

atoms	X-ray data for **9a**·2THF	calcd for **9b**·2OMe$_2$	atoms	X-ray data for **9a**·2THF	calcd for **9b**·2OMe$_2$
P(1)−N(1)	1.640(4)	1.642	P(1)−N(2)	1.640(4)	1.643
P(1)−N(3)	1.588(3)	1.611	P(1)−N(4)	1.716(3)	1.755
Al(1)−N(1)	1.911(5)	1.966	Al(1)−N(2)	1.886(4)	1.922
Li(1)−N(3)	1.969(7)	1.933	Li(1)−N(4)	2.178(7)	2.137
Al(1)−C(1)	1.980(5)	1.983	Al(1)−C(2)	1.989(5)	1.986
Li(1)−O(1)	1.993(8)	1.974	N(1)−Al(1)−N(2)	77.85(16)	76.8
N(3)−Li(1)−N(4)	71.6(2)	75.8	P(1)−N(4)−Li(1)	88.9(2)	86.0
P(1)−N(3)−Li(1)	100.6(3)	97.0	P(1)−N(1)−Al(1)	93.9(2)	93.4
P(1)−N(2)−Al(1)	94.9(2)	95.3	N(1)−P(1)−N(2)	93.3(2)	94.5
N(1)−P(1)−N(3)	121.63(19)	123.2	N(3)−P(1)−N(4)	94.71(16)	96.1

Scheme 1. Stepwise Deprotonation of Trisamino(imino)phosphates to Mixed Me$_2$Al$^+$/Li$^+$ Tetraimidophosphate Complexes and Subsequent Oxidation to Yield Persistent Spirocyclic Radicals (R = ^{t}Bu; R′ = SiMe$_3$, ^{t}Bu)



metrical tetraimidophosphate trianion [P(N^{t}Bu)$_4$]$^{3-}$ as the heterobimetallic complex {[Me$_2$Al][Li]$_2$[P(N^{t}Bu)$_4$]} was carried out by treating (^{t}BuNH)$_3$PN^{t}Bu first with AlMe$_3$, then with ^{n}BuLi. The structure of the THF adduct {Me$_2$Al[(μ-N^{t}Bu)$_2$P(μ_2-N^{t}Bu)$_2$(μ_2-THF)][Li(THF)]$_2$} (**11a**) was determined by X-ray crystallography. This complex crystallizes with a molecule of THF in its lattice, rendering the crystals unstable toward solvent loss once removed from solution. Consequently, the X-ray data are not of sufficient quality to allow for a discussion of the bond lengths and angles of this compound. However, the structural parameters are consistent with the corresponding parameters that were calculated for the model system {Me$_2$Al[(μ-NMe)$_2$P(μ_2-NMe)$_2$(μ_2-OMe$_2$)-[Li(OMe$_2$)]$_2$} (**11b**) (Table 4).



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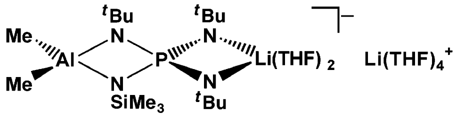


12

Complexes **10** and **11a** have been characterized by multinuclear (^{1}H, ^{7}Li, ^{13}C, and ^{31}P) NMR spectroscopy. The ^{1}H NMR spectrum of **10** in d_8-THF consists of two ^{t}Bu signals in a 1:2 ratio at 1.32 and 1.30 ppm, as well as singlets at 0.08 ppm and −0.94 ppm attributed to the SiMe$_3$ and AlMe$_2$ groups, respectively; the corresponding signals are observed in the ^{13}C NMR spectrum. While the expected singlet is observed at 10.0 ppm in the ^{31}P NMR spectrum, two resonances of approximately equal intensities are present in the ^{7}Li NMR spectrum at 1.44 and −2.71 ppm. The latter observation suggests that, in THF solution, solvation of one lithium cation occurs to produce the solvent-separated ion pair {[Li(THF)$_4$]}$^+${Me$_2$Al[(μ-N^{t}Bu)(μ-NSiMe$_3$)P(μ-N^{t}Bu)$_2$]-Li(THF)$_2$}$^-$ (**12**), comprised of a spirocyclic monoanion and a tetrasolvated lithium counterion. The related tetra(naphthylimido)phosphate {[Li(THF)$_4$]}$^+${Li(THF)$_2$[(μ-Nnaph)$_2$P-(μ-Nnaph)$_2$]Li(THF)$_2$]}$^-$ is known to have a spirocyclic structure in the solid state.[5]

In contrast, the NMR data obtained for **11a** in d_8-THF are consistent with its solid-state structure. The inequivalence of the two types of *tert*-butyl groups is not apparent from the ^{1}H NMR spectrum, since only a single ^{t}Bu resonance (1.34 ppm) is observed, accompanied by a singlet at −0.96 ppm attributed to the Me$_2$Al group. However, the ^{13}C NMR spectrum clearly shows two sets of ^{t}Bu signals (50.90 and 36.41 ppm; 50.78 and 34.45 ppm) with approximately equal intensities. The ^{7}Li NMR spectrum exhibits a singlet at 1.23 ppm, indicating the equivalence of the two lithium cations and, thus, that formation of a solvent-separated ion pair does not occur for **11a**.

Reactions of **3a** with AlMe$_3$ and ^{n}BuLi in THF are readily monitored by ^{31}P NMR spectroscopy, as a downfield shift is observed with each subsequent deprotonation of the ligand. The signal at −15 ppm for (^{t}BuNH)$_3$PNSiMe$_3$ disappears as the dimethylaluminum complex **4** forms (5.6 ppm). Initially, the addition of ^{n}BuLi results in the appearance of a peak at 8.2 ppm (**9a**); as more *n*-butyllithium is added, a signal for the dilithiated complex **12** is observed at 10.0 ppm. A similar trend in ^{31}P NMR chemical shifts is observed when **3a** is reacted with 1, 2, and 3 equiv of *n*-butyllithium.[11]

EPR and DFT Characterization of the Persistent Radicals {Me$_2$Al[(μ-NR)(μ-N^{t}Bu)P(μ-N^{t}Bu)$_2$]Li(THF)$_2$}$^\bullet$ (13a, R = SiMe$_3$; 14a, R = ^{t}Bu). When exposed to air, THF solutions of **12** turn a bright blue color, whereas solutions of **11a** become a deep teal color indicative of the formation of radicals. In earlier studies, we have isolated stable cubic tetraimidophosphate radicals by oxidization of the dimeric lithium salt {Li$_3$[P(N^{t}Bu)$_3$(NSiMe$_3$)]}$_2$ with 1 equiv of iodine or bromine.[25] Oxidations of the dimethyl-

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **11**

atoms	X-ray data for **11a**	calcd for **11b**	atoms	X-ray data for **11a**	calcd for **11b**
P(1)−N(1)	1.668(9)	1.661	Li(1)−O(1)	2.03(2)	1.960
P(1)−N(2)	1.671(9)	1.661	Li(1)−O(2)	2.15(2)	2.126
P(1)−N(3)	1.645(9)	1.668	Li(2)−O(2)	2.09(2)	2.126
P(1)−N(4)	1.597(10	1.668	Li(2)−O(3)	2.00(2)	1.960
Al(1)−N(1)	1.881(10)	1.918	N(1)−Al(1)−N(2)	77.4(4)	76.7
Al(1)−N(2)	1.877(10)	1.918	N(3)−P(1)−N(4)	91.7(5)	93.2
Li(1)−N(3)	2.07(2)	2.009	N(1)−P(1)−N(2)	89.4(5)	91.5
Li(2)−N(3)	2.01(2)	2.009	Li(1)−N(3)−P(1)	91.0(7)	86.4
Li(1)−N(4)	2.13(2)	2.009	Li(2)−N(4)−P(1)	91.1(7)	86.4
Li(2)−N(4)	1.98(2)	2.009	Li(1)−O(2)−Li(2)	67.1(8)	66.4

aluminum complexes **11a** and **12** are expected to yield neutral spirocyclic radicals via the elimination of 1 equiv of THF-solvated lithium halide (Scheme 1). In practice, the addition of 0.5 equiv of iodine to a colorless solution of **12** in THF results in an intense blue color, which persists for several hours in solution. In the solid state, this mixed heterobimetallic tetraimidophosphate radical **13a** is stable for only a few minutes; however, it has been identified by its solution EPR spectrum (Figure 3). The observed pattern is primarily a doublet due to coupling of the unpaired electron to the phosphorus atom (^{31}P, 100%, $I = {}^{1}/_{2}$), with a total of approximately 50 lines due to additional hyperfine coupling to the nitrogen (^{14}N, 99%, $I = 1$), lithium (^{7}Li, 92.5%, $I = 3/2$), and aluminum (^{27}Al, 100%, $I = 5/2$) nuclei.

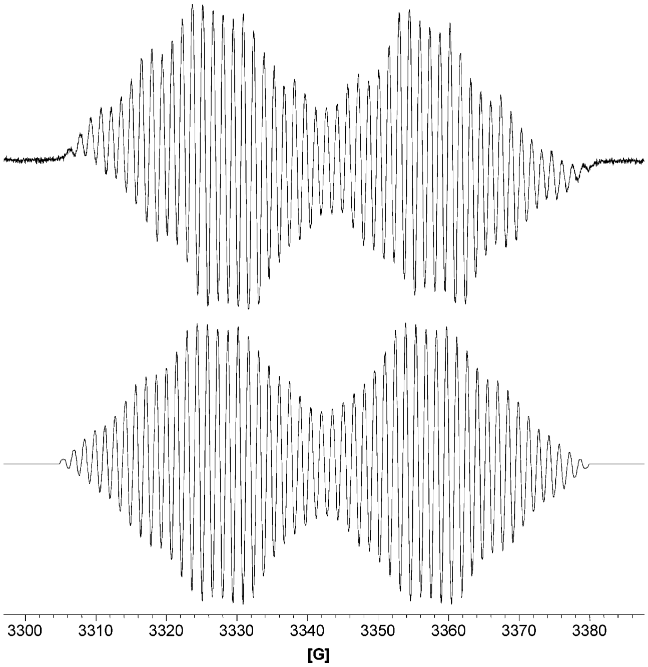
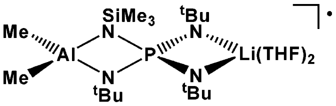
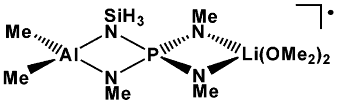


Figure 3. Experimental (top) and simulated (bottom) EPR spectra of **13a** in THF.



13a



13b

To aid in the interpretation of this complex spectrum, the model system $\{Me_2Al[(\mu\text{-}NMe)(\mu\text{-}NSiH_3)P(\mu\text{-}NMe)_2]Li(Me_2O)_2\}^\bullet$ (**13b**) was examined by means of DFT calculations. The optimized molecular structure displays C_s symmetry, with the AlN_2P and LiN_2P rings perpendicular to one another. The two NMe groups that chelate the lithium cation have equivalent P−N bond lengths of 1.668 Å, while slightly shorter P−N bond distances are observed for the remaining P−NMe unit (1.655 Å) and the P−$NSiH_3$ (1.650 Å) fragment. The four metal−nitrogen distances are quite similar, with an average N−Al bond length of 1.958 Å and identical Li−N distances (2.030 Å).

Single-point calculations on **13b** indicated that the singly occupied molecular orbital (SOMO) is primarily a linear combination of nitrogen p orbitals (Figure 4). For symmetry reasons, the contributions from the nitrogen atoms in the AlN_2P and LiN_2P rings are not equivalent; a Mulliken population analysis of the atomic spin densities revealed that the spin density is concentrated on the nitrogen atoms of the LiN_2P ring. Although the SOMO has only minor contributions from phosphorus, lithium, and aluminum, these atoms have nonzero spin densities owing to spin polarization effects. In consequence, the EPR spectrum of **13b**, and hence that of its parent system **13a**, is expected to show large hyperfine couplings to one phosphorus and two equivalent nitrogen atoms. Smaller couplings to the other two nitrogen atoms and the metal centers should also be present and are responsible for the extensive hyperfine structure seen in the experimental EPR spectrum. While the calculations indicate that the Me_2Al^+ cation also contributes to the SOMO, coupling to the methyl protons is expected to be so small as to be unobservable.

An excellent simulation of the experimental EPR spectrum was obtained by including hyperfine couplings to one phosphorus atom (29.29 G), one lithium cation (1.43 G), one aluminum atom (1.39 G), a pair of equivalent nitrogen nuclei (7.20 G), and two unique nitrogen atoms (1.61 and 0.27 G) (Figure 3). These hyperfine couplings are consistent with the retention of the spirocyclic arrangement of **12** upon oxidation and the formation of the neutral radical $\{Me_2Al[(\mu\text{-}N^tBu)_2P(\mu\text{-}N^tBu)_2]Li(THF)_2\}^\bullet$ (**13a**) (Scheme 1). To confirm the relative magnitudes of the HFCCs used to create the spectral simulation, the calculated data for **13b** were examined more closely. The differing spin densities on the

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(25) Armstrong, A.; Chivers, T.; Parvez, M.; Boeré, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 502−505.

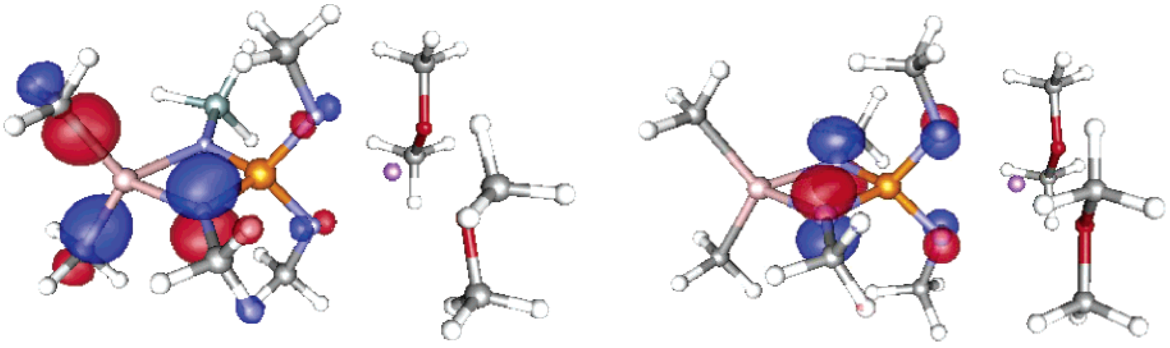


Figure 4. SOMO of **13b** (left) and **14b** (right).

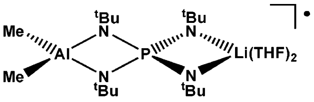
Table 5. Experimental and Calculated HFCCs (G) for **13** and **14**

nucleus	spin	**13a**[a]	**13b**[b]	**14a**[a]	**14b**[b]
^{27}Al	$^5/_2$	1.39	−1.22	1.99	−2.03
^{7}Li	$^3/_2$	1.43	−1.67	1.40	−1.58
^{31}P	$^1/_2$	29.29	−30.72	28.45	−30.96
^{14}N^{t}Bu···Li	1	7.20	6.61	6.44	5.76
^{14}N^{t}Bu···Al	1	1.61	−1.29	1.67	0.50
^{14}NSiMe$_3$	1	0.27	−0.07		

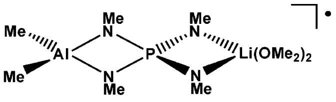
[a] Values used to simulate the experimental spectrum. [b] Values calculated for the model systems.

nitrogen atoms are reflected in the ^{14}N HFCCs, which were calculated to be largest for the two equivalent N^{t}Bu ligands that chelate the lithium cation (6.61 G), smallest for the NSiMe$_3$ group (−0.07 G), and of an intermediate size for the unique N^{t}Bu nitrogen atom (−1.29 G). The calculated HFCCs are shown in Table 5, along with the values used to create the spectral simulation shown in Figure 3. The largest calculated HFCC was to the phosphorus nucleus (−30.72 G), while the much smaller aluminum (−1.22 G) and lithium (−1.67 G) couplings are calculated to be fairly similar. These calculated HFCCs provide good support for the proposed spirocyclic structure of the radical **13a**.

The one-electron oxidation of **11a** with halogens yields the persistent teal radical {Me$_2$Al[(μ-N^{t}Bu)$_2$P(μ-N^{t}Bu)$_2$]Li(THF)$_2$}$^\bullet$ (**14a**) with a stability similar to that of **13a**: it persists in solution for approximately 3 h but cannot be isolated in the solid state. The solution EPR spectrum of this radical is shown in Figure 5. DFT calculations were carried out on the model system {Me$_2$Al[(μ-NMe)$_2$P(μ-NMe)$_2$]Li(Me$_2$O)$_2$}$^\bullet$ (**14b**). The geometry-optimized structure of this molecule has C_{2v} symmetry, with the two MN$_2$P (M = Li, Al) rings perpendicular to one another. The two pairs of P−N bond lengths in this structure are equivalent within the accuracy of the calculations, at 1.650 and 1.653 Å for the P−N−Al and P−N−Li distances, respectively. As was seen for **13b**, the Al−N bonds (1.936 Å) are slightly shorter than the Li−N bonds (1.984 Å).



14a



14b

Further examination of the data indicated that the composition of the SOMO (Figure 4) of **14b** is similar to that of **13b**. An excellent simulation of the experimental EPR spectrum was obtained by including hyperfine couplings to two pairs of equivalent ^{14}N atoms (6.44 G, 1.67 G), one lithium cation (1.40 G), one dimethylaluminum cation (1.99 G), and the phosphorus atom (28.45 G). The close agreement of the experimental and calculated HFCCs, which are shown in Table 5, confirms that the oxidation product of **11a** is indeed the neutral spirocycle radical {Me$_2$Al[(μ-N^{t}Bu)$_2$P(μ-N^{t}Bu)$_2$]Li(THF)$_2$}$^\bullet$ (**14a**). Unlike other related tetraimidophosphate radicals,[25] the EPR spectra of **13a** and **14a** are not dependent on sample concentration, indicating that dissociation of these spirocyclic radicals (e.g., by solvation of the lithium cations) does not occur even in very dilute solutions.

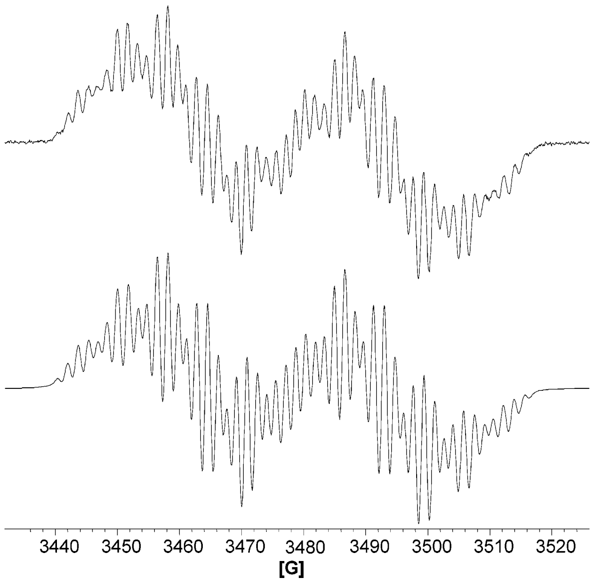
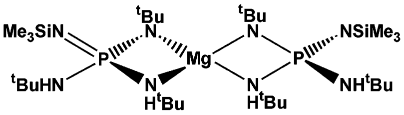


Figure 5. Experimental (top) and simulated (bottom) EPR spectra of **14a** in THF.

Synthesis and Characterization of {Mg[(μ-N^{t}Bu)(μ-NH^{t}Bu)P(NH^{t}Bu)(NSiMe$_3$)]$_2$} (15), {Mg[(μ-NCy)(μ-NSiMe$_3$)P(NHCy)$_2$]$_2$} (16), {Mg[(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]$_2$} (17), and {[MgOH][(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]}$_6$ (18). The reaction of MgBu$_2$ with 2 equiv of (^{t}BuNH)$_3$PNSiMe$_3$ (**3a**) produces a complex in which a magnesium dication is bis-chelated by two imidophosphate monoanions {Mg[(μ-N^{t}Bu)(μ-NH^{t}Bu)P(NH^{t}Bu)(NSiMe$_3$)]$_2$} **15**. This compound has been characterized by multinuclear NMR spectroscopy and displays a single resonance in its ^{31}P spectrum at 5.2 ppm. The ^{1}H NMR spectrum of **15** in C$_6$D$_6$ is interesting in that it consists of three ^{t}Bu signals of equal intensities, one SiMe$_3$

resonance, and two broad doublets that are attributable to two inequivalent NH protons. These data indicate that the imidophosphate ligand is coordinated to the magnesium atom through one NH^{t}Bu and one N^{t}Bu group. This is somewhat surprising, considering the well-established structures of the dimethylaluminum complexes **4**, **9a**, **10**, and **11a**, in which the aluminum atom is chelated by the two imido groups, while the amido substituents remain noncoordinated. This preference is attributed to the fact that Mg^{2+} is a harder acid than Me$_2$Al$^+$ and will, therefore, prefer coordination to the harder base NH^{t}Bu over coordination to the NSiMe$_3$ nitrogen atom.



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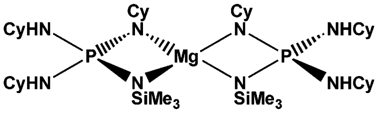

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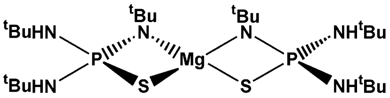
The reaction of MgBu$_2$ with the cyclohexyl derivative (CyNH)$_3$PNSiMe$_3$ (**3b**) in a 1:2 molar ratio produces a complex that was identified as {Mg[(μ-NCy)(μ-NSiMe$_3$)P(NHCy)$_2$]$_2$} (**16**) on the basis of NMR data and CHN analysis. The appearance of resonances for only two cyclohexyl environments in a 2:1 ratio in the ^{13}C NMR spectrum (in C$_6$D$_6$) suggests coordination of two imido groups (NSiMe$_3$ and NCy) to the magnesium center and two exocyclic cyclohexylamido groups.

Attempts to effect further deprotonation by changing the reaction conditions and stoichiometry were unsuccessful; the only products observed by ^{31}P NMR were the monoanionic complexes **15** and **16**. Similar low reactivities were observed for these species toward dimethylzinc and trimethylaluminum. However, the trisamino(thio)phosphate SP(NH^{t}Bu)$_3$ (**2a**) was previously found to be slightly more reactive than (RNH)$_3$PNSiMe$_3$ toward ZnMe$_2$.[7] Consequently, reactions between MgBu$_2$ and **2a** were explored using various stoichiometries and reaction conditions.

When 0.5 equiv of MgBu$_2$ was employed, a white powder was recovered that gave rise to only one ^{31}P NMR signal (38.8 ppm). The ^{1}H NMR and ^{13}C NMR spectra of the product in C$_6$D$_6$ indicated the presence of two inequivalent ^{t}Bu environments. The 1:2 integration of the ^{1}H NMR peaks (at 1.56 and 1.45 ppm), and the absence of any resonances attributable to a BuMg$^+$ cation, is consistent with the formation of the *N*,*S*-chelated complex {Mg[(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]$_2$} (**17**).



17

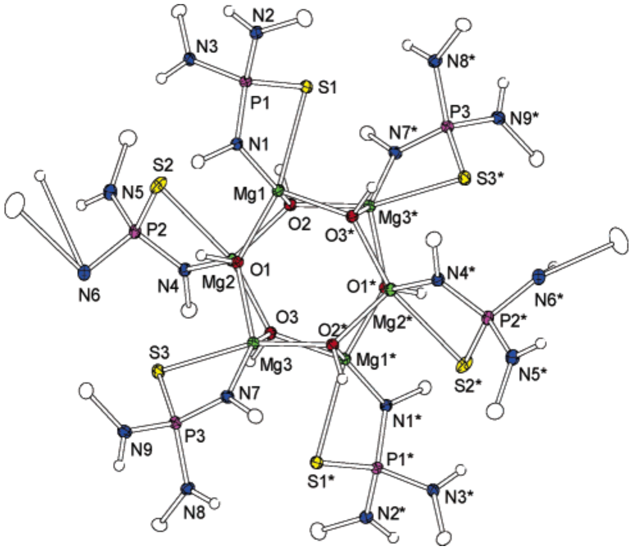


Figure 6. Thermal ellipsoid diagram of **18** (30% probability ellipsoids). Only α-carbons of the *tert*-butyl groups are shown.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **18**[a]

P(1)−N(1)	1.6078(16)	P(1)−N(2)	1.6532(17)
P(1)−N(3)	1.6721(18)	P(1)−S(1)	2.0112(8)
Mg(1)−O(1)	2.0266(15)	Mg(1)−O(2)	2.1191(15)
Mg(1)−O(3)	2.0030(16)	Mg(2)−O(1)	2.1198(15)
Mg(2)−O(2)	2.0042(15)	Mg(2)−O(3)	2.0325(15)
Mg(3)−O(1)	2.0039(15)	Mg(3)−O(2)	2.0346(16)
Mg(3)−O(3)	2.1208(15)	Mg(1)−N(1)	2.0675(17)
Mg(1)−S(1)	2.6290(10)	Mg(2)−N(4)	2.0686(18)
Mg(2)−S(2)	2.6166(11)	Mg(3)−N(7)	2.0677(18)
Mg(3)−S(3)	2.6237(11)	Mg(1)−Mg(2)	3.0317(12)
N(2)−P(1)−N(3)	100.60(9)	P(1)−S(1)−Mg(1)	75.56(3)
P(1)−N(1)−Mg(1)	102.69(8)	S(1)−Mg(1)−N(1)	74.47(5)
O(1)−Mg(1)−O(2)	83.08(6)	Mg(1)−O(1)−Mg(2)	93.94(6)
S(1)−P(1)−N(1)	104.74(6)	O(1)−Mg(3)−O(2*)	103.21(6)
O(2)−Mg(2)−O(3)	102.40(6)	O(1)−Mg(2)−O(2)	83.60(6)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 1$, $-z$.

Attempts to grow single crystals of **17** from a variety of organic solvents were unsuccessful; however, it was found that prolonged storage of this complex in Et$_2$O leads to the of the hexameric complex {[Mgμ_3-OH][(μ-S)(μ-N^{t}Bu)P(NH^{t}Bu)$_2$]}$_6$ (**18**), presumably via the partial hydrolysis of **17**. An X-ray structure of **18** (Figure 6) revealed that the core of this complex is composed of six [Mgμ_3-OH]$^+$ cations linked together via Mg−O bonds to form two stacked six-membered Mg$_3$O$_3$ rings (or a Mg$_6$O$_6$ hexagonal prism). Each magnesium center is also *N*,*S*-chelated by the monoanionic ligands [SP(NH^{t}Bu)$_2$(N^{t}Bu)]$^-$, rendering the Mg^{2+} cations pentacoordinate. The bis(amido)imido(thio)phosphate ligands radiate outward from the Mg$_6$O$_6$ core, with the two ^{t}BuNH groups of each ligand remaining noncoordinated. Selected bond lengths and bond angles for **18** are summarized in Table 6. The three Mg−O bonds in the center of the molecule are inequivalent: each magnesium atom has one short bond [e.g., Mg(1)−O(3) = 2.0030(16) Å], which can be considered a discrete [MgOH]$^+$ unit; one slightly weaker bond [Mg(1)−O(1) = 2.0266(15) Å] to a second oxygen atom within a Mg$_3$O$_3$ ring; and a third, longer distance [Mg(1)−O(2) = 2.1191(15) Å] between the magnesium of one Mg$_3$O$_3$ ring and an oxygen atom in the other six-membered ring. The average Mg−O bond distance in **18** is 2.054(15) Å, compare 1.9473(13)−2.0020(14) Å for the related complex {[NaMg-

Table 7. Reactivities of $EP(NHR)_3$ toward Metal Alkyl Reagents MR_x

(E, R)	^{n}BuLi	$ZnMe_2$	$AlMe_3$	$MgBu_2$
O, ^{t}Bu	1- or 2-fold deprotonation[a]	3-fold deprotonation; multiple products formed[b]	1- or 2-fold deprotonation[c]	Possibly 3-fold deprotonation; multiple products formed[d]
S, ^{t}Bu	1- or 2-fold deprotonation; sulfur extrusion and dimerization to a metaphosphate[e]	monodeprotonation[b]	1- or 2-fold deprotonation[d]	monodeprotonation; sulfur extrusion at high temperatures[d]
$NSiMe_3$, Cy	3-fold deprotonation[f]	monodeprotonation[b]	dimerization to metaphosphate[d]	monodeprotonation; NCy, $NSiMe_3$ chelation[d]
$NSiMe_3$, ^{t}Bu	3-fold deprotonation[f]	monodeprotonation; N^{t}Bu, $NSiMe_3$ chelation[b]	monodeprotonation; N^{t}Bu, $NSiMe_3$ chelation[d]	monodeprotonation; N^{t}Bu, NH^{t}Bu chelation[d]

[a] References 6 and 8. [b] Reference 7. [c] Reference 12. [d] This work. [e] References 8 and 10. [f] Reference 6.

$(N^{i}Pr)_2(O)\cdot THF\}_6$, which also contains a core of two stacked Mg_3O_3 rings.[26] The bis(amido)imido(thio)phosphate ligand, as expected, contains one short P−N bond to the *tert*-butylimido nitrogen atom [P(1)−N(1) = 1.6078(16) Å], while longer distances are observed to the two *tert*-butylamido groups [P(1)−N(2) = 1.6532(17) Å; P(1)−N(3) = 1.6721(18) Å].

The deliberate hydrolysis of **17** with 1 equiv of H_2O was attempted in both diethyl ether and toluene. Reaction times of more than 10 min result in the complete hydrolysis of **17**, and a mixture of $SP(NH^{t}Bu)_3$ (**2a**) and magnesium oxide was recovered. Over shorter reaction times, two signals of equal intensity attributable to **2a** and **17** are observed in the ^{31}P NMR spectrum of the product mixture. It is thought that removal of the solvent under a vacuum facilitates the loss of water from **18** so that the hydroxide complex is not observed.

The reaction of **2a** and $MgBu_2$ in a 1:1 stoichiometry gave a complex mixture of products, as revealed by ^{31}P NMR spectra. The marked increase in the number of products formed from the reaction of $EP(NH^{t}Bu)_3$ (E = O, S) with dibutylmagnesium as compared to dimethylzinc[7] can be attributed to the higher electrophilicity of the magnesium cations and their tendency to adopt octahedral rather than tetrahedral coordination modes.

Conclusions

The trisamidophosphates $EP(NHR)_3$ (E = O, S, NR′; R = alkyl) display similar reactivities toward $AlMe_3$ as they do toward $ZnMe_2$, with the highest reactivity observed for E = O and the lowest reactivity for E = NR′. Three-fold deprotonation of these species to form imido analogues of the well-known aluminophosphates does not occur. In the case of E = NR′, two different reaction pathways can occur to yield imido analogues of *ortho*- or *meta*-phosphate, depending on the identity of the R group employed. Reactions of $AlMe_3$ with $SP(NH^{t}Bu)_3$ yield *N*,*S*-chelated complexes. Lithiation of aluminum bis(amido)bis(imido)phosphates produces heterobimetallic complexes that form persistent radicals upon oxidation with iodine. Reactions with $MgBu_2$ lead to multiple products for E = O and S, but only a simple monoanionic complex of E = NR′. The different behaviors of **1**−**3** toward various organometallic (metal alkyl) reagents are summarized in Table 7.

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Supporting Information Available: Crystallographic CIF files are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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